

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-212229

(43)Date of publication of application : 02.08.2000

(51)Int.Cl.

C08F220/56

C08F 2/00

D21H 17/54

(21)Application number : 11-017854

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(22)Date of filing : 27.01.1999

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(54) ADDITIVE FOR PAPER-MAKING AND ITS PREPARATION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a preparation process of a water-soluble polymer having a high molecular weight and a low viscosity, wherein polymerization is easily controlled, and the obtained polymer exerts excellent effects on the paper force and water-filtering property and a high stability against condition fluctuations as an additive for paper-making.

SOLUTION: This additive is prepared by copolymerizing (a) from 50 to 99.75 mol% acrylamide and/or methacrylamide, (b) from 0.1 to 20 mol% water-soluble anionic monomer and/or (c) from 0.1 to 20 mol% water-soluble cationic monomer and (d) from 0.05 to 10 mol% methacrylonitrile as constituents.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

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CLAIMS

[Claim(s)]

[Claim 1] (a) The water-soluble polymer characterized by coming to copolymerize (b) water solubility anionic monomer 0.1 - 20-mol % and/or (c) water solubility cationic monomer 0.1 - 20-mol % and (d) methacrylonitrile 0.05 - ten-mol % as a constituent acrylamide and/or 50-99.75 mol% of meta-acrylamides.

[Claim 2] The water-soluble polymer according to claim 1 characterized by furthermore containing a cross-linking monomer as a copolymerization component.

[Claim 3] Claim 1 characterized by using a chain transfer agent, and a water-soluble polymer according to claim 2.

[Claim 4] (a) The manufacture approach of the additive for paper manufacture characterized by adding and carrying out the polymerization of the catalyst to the monomer mixed water solution which consists of (b) water solubility anionic monomer 0.1 - 20-mol % and/or (c) water solubility cationic monomer 0.1 - 20-mol % and (d) methacrylonitrile 0.05 - ten-mol % acrylamide and/or 50-99.75 mol% of meta-acrylamides.

[Claim 5] The manufacture approach according to claim 4 chosen from the group which a catalyst becomes from a peroxide catalyzer, a persulfate catalyst, a bromate catalyst, a fault boron acid chloride catalyst, a redox system catalyst, and an azo system catalyst.

[Claim 6] The manufacture approach according to claim 4 to which the polymerization of the catalyst is further added and carried out after performing addition of a catalyst in 2 steps, adding and carrying out the polymerization of the first catalyst to a monomer mixed water solution and making a prepolymer form.

[Claim 7] The manufacture approach according to claim 6 that the catalyst to add is persulfate.

[Claim 8] The additive for paper manufacture which makes an active principle a water-soluble polymer according to claim 1.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] About the additive for paper manufacture which uses a water-soluble polymer suitable as an additive for paper manufacture, and this water-soluble polymer as a principal component, this invention relates to the water-soluble polymer which forms the water solution of hypoviscosity, and its manufacture approach, though it is especially the amount of macromolecules. The acrylamide system polymer of this invention is useful especially as an additive which demonstrates the effectiveness excellent in the paper durability enhancing effect which can be set like a paper maker.

[0002]

[Description of the Prior Art] It sets in the paper manufacture industry conventionally, and the acrylamide system polymer is used for various applications as a paper reinforcing agent, a filtration improvement agent, a yield improver, and a flocculant. In recent years, as part of energy saving measures and an environmental cure, ** as a paper maker progresses and paper-milling conditions are changing to a raise in electrical conductivity, a raise in pH, and elevated-temperature-ization more. Furthermore, improvement in the speed of a machine, a limit of the appending rate of a sulfuric-acid band, etc. come to be made for the purpose of improvement in productivity, it has become a situation with the conventional chemical inadequate [the improvement effectiveness in paper durability], and the bottom of such a condition is asked for the applicable paper reinforcing agent.

[0003] As what replies to such a request, the water-soluble copolymer of the both sexes of acrylamide, alpha, and beta-partial saturation monochrome or dicarboxylic acid, and the basic monomer like dimethylaminoethyl methacrylate is proposed (JP,54-30913,A, JP,60-94697,A). However, in the both-sexes copolymer of these former, although a certain amount of improvement is found, it cannot be satisfied, and development of the drugs which can demonstrate much more effectiveness was desired.

[0004] Then, by introducing the structure of cross linkage and branching structure into polymer structure, macromolecule quantification is carried out suppressing a viscosity rise of a solution, and the attempt which aims at improvement in the engine performance is made. such a polymer -- by improving from a structural field, the more stable chemical effectiveness came to be acquired to fluctuation of paper-milling conditions.

[0005] As an example proposed until now, what uses the monomer which has two or more double bond parts (JP,63-50597,A, JP,4-18190,A), and the thing (JP,3-227489,A, JP,6-41898,A) which used the reactant monomer as a cross linking agent are in a molecule as a cross linking agent. Moreover, use (JP,8-67715,A) of the approach (JP,5-272092,A, JP,5-287693,A, JP,5-140892,A, JP,7-97790,A) and allyl compound system monomer which use N-permutation acrylamide derivative as a cross linking agent etc. is proposed. However, each of these has the fault that it is difficult gelation or to hypoviscosity-be easy toize and to control a polymerization to stability, according to polymerization conditions.

[0006]

[Problem(s) to be Solved by the Invention] This invention is faced obtaining the acrylamide

system polymer of the letter of branching which is hypoviscosity though it is the same amount of macromolecules as what is depended on the conventional technique, a polymerization reaction can be controlled more to stability, and the additive for paper manufacture which makes an active principle the polymer which made branching structure homogeneity by this, and demonstrates stable effectiveness to the outstanding paper durability improvement effect and condition fluctuation is offered.

[0007]

[Means for Solving the Problem] this invention persons came to complete a header and this invention for attaining the purpose by using the acrylamide system copolymer obtained by copolymerizing the monomer mixture which contains the methacrylonitrile which shows the chain transfer effectiveness and the bridge formation effectiveness as an indispensable component, as a result of repeating research wholeheartedly, in order to develop the additive for paper manufacture with the stable effectiveness of opposite *Perilla frutescens* (L.) Britton var. *crispa* (Thunb.) Decne. to the water quality of service water, or fluctuation of paper milling pH.

[0008] That is, it is the additive for paper manufacture obtained by copolymerizing (b) water solubility anionic monomer 0.5 - 20-mol % and/or (c) water solubility cationic monomer 0, 5 - 20-mol % and (d) methacrylonitrile 0.05 - ten-mol % monomer mixture (a) acrylamide and/or meta-acrylamide 50 - 9.75-mol%.

[0009] In this invention, the acrylamide or methacrylamide which is the (a) component may be used independently, and may use both together.

[0010] (b) As an example of the water-soluble anionic monomer of a component, the thing of sulfonic-acid systems, such as dicarboxylic acid systems, such as monocarboxylic acid systems, such as an acrylic acid, a methacrylic acid, and a crotonic acid, a maleic acid, a phthalic acid, an itaconic acid, and a citraconic acid, a vinyl sulfonic acid, a styrene sulfonic acid, and 2-acrylamido-2-methyl propane sulfonic acid, is mentioned. This monomer may be a salt and can mention the sodium salt of the various above-mentioned organic acids, potassium salt, etc. as a salt. In addition, these may be used independently, and may mix and use two or more kinds.

[0011] (c) Acrylamide (meta) derivatives, such as acrylic ester (meta) derivative [, such as dialkyl aminoethyl (meta) acrylate which is the monomer which has the third class amino group as an example of the water-soluble cationic monomer of a component, and dialkyl aminopropyl (meta) acrylate,], dialkyl aminopropyl (meta) acrylamide, dialkyl aminopropyl (meta) acrylamide, and acrylamide (meta)-3-methylbutyl dimethylamine, can be mentioned.

[0012] In addition, the water-soluble cationic monomer of (c) The salt of MOMA which has the above-mentioned third class amino group may be used. As such a salt A salt with an inorganic acid like a hydrochloric acid and a sulfuric acid is sufficient, and a salt with an organic acid like a formic acid and an acetic acid is sufficient, and Furthermore, the quaternary salt which formed the third class amino group into 4 class by methyl chloride, low-grade alkyl halide like a methyl bromide, benzyl chloride, aralkyl halide like benzyl bromide, the dimethyl sulfate, epichlorohydrin, etc. is sufficient. Moreover, these (c) components may be used independently, and two or more kinds may be mixed and they may be used.

[0013] the quantitative relation of each above component -- (a) component 99.75 - 50-mol % -- desirable -- 98.9 - 65-mol %, (b) component 0.1 - 20-mol % -- desirable -- 0.5 - 15-mol %, (c) component 0.1 - 20-mol % -- desirable -- 0.5 - 15-mol %, (d) component 0.05 - ten-mol % -- it is 0.1 - five-mol % preferably.

[0014] this invention -- setting -- everything but indispensable component (a) - (d) -- the purpose of this invention -- there -- it is 7, and it is the range and other monomers can be made to contain As such a monomer, there are diacetone acrylamide, acrylic nitril, alkyl acrylate, hydroxy acrylate, vinyl acetate, styrene, alpha methyl styrene, etc. the total mol sum of the monomer component constituted although the amount of these monomers used changes with properties of each monomer and does not generally have ***** -- receiving -- about 0.1-40 mol % -- it is preferably good about 0.5-30 mol %.

[0015] In this invention, although a cross linking agent is not necessarily needed since the bridge formation effectiveness is done so by the methacrylonitrile itself, it is the range which does not spoil the purpose of this invention, and it is possible to use other cross linking agents together if

needed. As such a cross linking agent For example, methylenebis Acrylamide, an ethylene screw (Meta) 2 functionality cross linking agents, such as acrylamide, ethylene GURIKORUJI (meta) acrylamide, diethylene GURIKORUJI (meta) acrylamide, TORIECHIRENGURIKORUJI (meta) acrylamide, a divinylbenzene, and diaryl acrylamide, (Meta) Or polyfunctional cross linking agents, such as 1, 3, 5-thoria chestnut roil hexahydro-S-triazine, triallyl isocyanurate, thoria krill acid pentaerythritol, trimethylol propane acrylate, and diacryloyl imide, N-permutation acrylamide system monomers, such as dimethyl acrylamide, diacetone acrylamide, and isopropyl acrylamide, are mentioned.

[0016] Although the amount used is an amount usually smaller than conditions, and ends and it is 0.005-3-mol % to the total amount of all monomers in order that the bridge formation effectiveness by the methacrylonitrile itself may work, although these cross linking agents can carry out concomitant use use of one sort or the two sorts or more, it is 0.01-1-mol % preferably.

[0017] Moreover, in this invention, although a chain transfer agent is not necessarily needed in order to also commit the chain migration effectiveness by the methacrylonitrile itself, it is possible to use other chain transfer agents together if needed in the range which does not spoil the purpose of this invention. As an example of such a chain transfer agent, the thing of allyl compound systems, such as mercapto systems, such as mercaptoethanol besides isopropyl alcohol, thiourea, thioglycolic acid, mercaptopropionic acid, thiosalicylic acid, thiolactic acid, an aminoethane thiol, thioglycerol, and thiomalic acid, allyl alcohol, allyl compound sulfonic-acid soda, and meta-allyl compound sulfonic-acid soda, is mentioned. in order that these chain transfer agents can carry out concomitant use use of one sort or the two sorts or more and may also commit the chain transfer effectiveness by the methacrylonitrile itself as mentioned above -- an amount with less amount used than this usual kind of reaction condition -- it is -- ending -- the total amount of all monomers -- receiving -- about 0.01-5 mol % -- it is preferably good about 0.03-2 mol %.

[0018] In this invention, various well-known approaches are conventionally applicable as a polymerization method for obtaining a water-soluble polymer. For example, in addition to this, a monomer, a cross linking agent, a chain transfer agent, and water can be taught to a predetermined reaction container said various monomers ((a) - (b) component) and if needed, a polymerization initiator can be added, and the water-soluble target polymer (this may be hereafter called a water-soluble copolymer and a copolymer water solution) can be obtained by warming under stirring. Moreover, while a part or all of a monomer is dropped into a reaction container, it may be made to carry out a polymerization. A catalyst injection can obtain the polymer of the high amount of macromolecules of whenever [branching] by adding a catalyst, although at least 1 time is possible.

[0019] Reaction temperature is about 40-100 degrees C, and reaction time is usually about 0.5 - 8 hours. If it is the radical polymerization initiator usually used in a water solution as a polymerization initiator, it can be used that there is especially no limit, for example, a catalyst is a hydrogen peroxide, a benzoyl peroxide, a peroxide catalyzer like t-butyl peroxide, and persulfuric acid. A bromate catalyst like a persulfate catalyst like ammonium, sodium persulfate, and potassium persulfate, sodium bromate, and a potassium bromate and a fault boron acid chloride catalyst like fault boron acid sodium are mentioned. Moreover, the redox system catalyst and azo system catalyst which combined the sulfite, the hydrogensulfite, the transition-metals salt, the organic amine, etc. with these as a reducing agent can also be used. These may be used independently and may be used combining two or more kinds. the amount of these catalysts used -- the AUW of a monomer -- receiving -- about 0.01-10wt% -- it is about 0.05-3wt% preferably.

[0020] Also about an additional catalyst, although the same thing as a catalyst is usable for a start (the 1st step), it sees from catalyst effectiveness and a cost side, for example, persulfate like ammonium persulfate or sodium persulfate is the optimal. Of course, especially when there are many amounts of survival of the catalyst used for the 1st step, it is not necessary to add. It is 70-95 degrees C often [temperature / the temperature in the case of carrying out the additional polymerization of the prepolymer is 40 degrees C or more, and / making about 15-55

degrees C / reaction / the 1st step of / into an elevated temperature], and preferably, the amount of the additional catalyst used -- 0.01 - 10wt% -- it is 0.05 - 3wt% preferably. A monomer can also be added to this additional catalyst and coincidence if needed. This monomer presentation may be the same as an initial preparation monomer presentation, or may differ.

[0021] In this invention, while resonance stabilization of the radical generated according to the radical catalyst is carried out by the nitrile group of a methacrylonitrile and it carries out chain transfer-work, by forming the point by the abstraction reaction from a methyl group constructing a bridge, it has work of a cross linking agent/chain transfer agent by the methacrylonitrile independent, and does not have generating of rapid thickening, either, and it becomes easy to polymerization control it.

[0022] In addition, the additive for paper manufacture of this invention can introduce branching structure into a polymer, and serves as hypoviscosity comparatively like ** and the acrylamide system polymer of a conventionally well-known bridge formation mold. Usually, although it is compoundable in the range of 5 - 40 % of the weight of solid content concentration, when using it as an additive for paper manufacture, it is desirable to use it by description 15000cps or less, and 5 - 30% of the weight of the range is desirable as solid content concentration. Therefore, the amount of the water used for a polymerization reaction is good to refer to this and to determine it suitably.

[0023] When it is used as an additive for paper manufacture, the copolymer not only demonstrates the paper durability effectiveness and effectiveness high in respect of filterability, but demonstrates stable effectiveness to condition fluctuation of a paper-milling system, while it is the description to obtain easily the copolymer water solution in which hypoviscosity is shown, though this invention is the amount of macromolecules.

[0024]

[Embodiment of the Invention] An example and the example of a comparison are given to below, and this invention is more concretely explained to it. In addition, each of sections and %s is weight criteria as long as there is no special mention.

[0025]

[Example 1] The 50% acrylamide water-solution 256 section, the acrylic-acid 5.8 section, the dimethylaminoethyl methacrylate 3.2 section, the meta-KURORU nitril 1.4 section, and the water 270 section were taught to the 4 opening flask equipped with an agitator, a thermometer, a ring current cooling pipe, and nitrogen gas installation tubing, pH was adjusted to 3.2 with the sulfuric acid, and the oxygen in the system of reaction was removed through nitrogen gas. The inside of a system was made into 40 degrees C, and the ammonium persulfate water-solution 3.4 section and the 1% sodium-hydrogensulfite water-solution 6 section were supplied 10% as a catalyst to the bottom of stirring. After carrying out a temperature up to 90 degrees C, the ammonium persulfate water-solution 3 section was added 10 more%, and temperature was held for 2 hours. The water 110 section was supplied after reaction termination, and the copolymer water solution of pH 3.7, the solid content of 15.4%, the viscosity (25 degrees C) of 7600cps, and weight average molecular weight 2,340,000 was obtained.

[0026]

[Example 1-a] The monomer mixed water solution adjusted like the example 1 was made into 40 degrees C, and the 10% water-solution 5 of 2 of azo system catalyst and 2'-azobis (2-amidinopropane) hydro chloride section was supplied as a catalyst. After solution temperature amounted to 85 degrees C or more, the ammonium persulfate water-solution 4 section was added 10 more%, and this temperature was held for 2 hours. The water 110 section was supplied after reaction termination, and the copolymer water solution of pH4.0, the solid content of 15.7%, the viscosity (25 degrees C) of 8200cps, and weight average molecular weight 2,480,000 was obtained.

[0027]

[Example 1-b] The monomer mixed liquor adjusted like the example 1 was made into 40 degrees C, and the ammonium persulfate water-solution 6 section was supplied 10% as a catalyst. Solution temperature was held above 85 degrees C for 2 hours. The water 110 section was supplied after reaction termination, and the copolymer water solution of pH3.9, the solid content

of 15.6%, the viscosity (25 degrees C) of 4800cps, and weight average molecular weight 1,890,000 was obtained.

[0028]

[Examples 2-10] In the example 1, the class or its operating rate of (a) - (d) component was changed as shown in Table 1, and also the same actuation as an example 1 was performed, and various copolymer water solutions were obtained. the description of the obtained various copolymer water solutions -- Table 2 is shown for a value.

[0029]

[Table 1]

	モノマーの種類および使用割合 (モル%)					架橋剤(d) (モル%)	連鎖移動剤 (モル%)
	(a)成分	(b)成分	(c)成分	成分			
実施例 1	AM 90	AA 4	DM 5	MAN 1			
実施例 2	AM 91.5	IA 3	DMBQ 5	MAN 0.5			IPA 1
実施例 3	AM 92	AA 2	DM 1	MAN 1	MBAM 0.01		
		FA 1	DMBQ 3				
実施例 4	AM 91.6	IA 1	DMAPAA 4	MAN 1.4	DMAM 0.05		
		AA 2					
実施例 5	AM 89	AA 2	DM 3	MAN 2	MBAM 0.01	AS 0.6	
		MA 2	DMBQ 2				
実施例 6	AM 91.7	FA 3	DM 5	MAN 0.3	MBAM 0.02	IPA 2	
実施例 7	AM 88.8	IA 3	DMBQ 6	MAN 1.2	DMAM 0.1	MAS 0.05	
		FA 1					
実施例 8	AM 93.5	IA 2	DM 3.5	MAN 1	DMAM 0.1	AS 0.4	
実施例 9	AM 89.3	AA 3	DM 2	MAN 0.7	DMAM 0.2	IPA 2	
		FA 3	DMBQ 4				
実施例 10	AM 93.8	IA 1	DMBQ 3	MAN 1.2	MBAM 0.02	MAS 0.1	
		MA 1					
比較例 1	AM 92	AA 3	DM 5			IPA 3	
比較例 2	AM 93	AA 1	DMBQ 4		MBAM 0.06	IPA 5	
		IA 2					
比較例 3	AM 93	IA 2	DMAPAA 3		DMAM 1	AS 1.2	
		FA 1	DM 1				
比較例 4	AM 91	AA 2	DM 3		DMAM 0.7	MAS 0.4	
		MA 2	DMBQ 2				

[0030]

[The examples 1-4 of a comparison] Moreover, as examples 1-4 of a comparison, the class or its operating rate of (a) - (d) component of an example 1 was changed, as shown in the example of a comparison of Table 1, and also the same actuation as an example 1 was performed, and various copolymer water solutions were obtained. In addition, although the examples 2-4 of a comparison tended to obtain the object 5000cps or more of product viscosity, since they lifting-came to be easy of rapid thickening and gelation in the second half of a polymerization, they performed viscosity control in the amount of catalysts etc., and obtained the product. the description of the obtained various copolymer water solutions -- Table 2 is shown for a value.

[0031]

[Table 2]

	性 状			
	固形分 (%)	pH	粘度 (cps)	Mw (万)
実施例 1	15.4	3.7	7600	234
実施例 2	15.7	3.9	8700	213
実施例 3	15.2	4.3	9300	257
実施例 4	15.5	4.0	11100	267
実施例 5	15.6	4.1	7600	243
実施例 6	15.3	3.8	3500	231
実施例 7	15.6	3.7	9200	276
実施例 8	15.4	3.9	12300	278
実施例 9	15.3	4.0	7100	226
実施例 10	15.4	4.1	4300	225
比較例 1	15.3	4.0	7800	43
比較例 2	15.4	3.9	3200	165
比較例 3	15.6	4.3	3800	213
比較例 4	15.3	4.1	2800	243

As front Naka and a (a) component, as an AM:acrylamide and (b) component AA:acrylic acid, As an itaconic acid, FA:fumaric acid, and an MA:maleic-acid and (c) component, IA : DM:dimethylaminoethyl methacrylate, As dimethylaminopropyl acrylamide, the fourth class ghost by the benzyl chloride of DMBQ:DM, and a (d) component, DMAPAA : as MAN:meta-KURORU nitril and a cross-linking monomer MBAM: Methylenebis acrylamide, DMAM: IPA:isopropyl alcohol, MAS:meta-allyl compound sulfonic-acid soda, and AS:allyl compound sulfonic-acid soda are shown as dimethyl acrylamide and a chain transfer agent, respectively.

[0032]

[Performance evaluation] corrugated paper used paper -- a Niagara style -- beating was carried out with the beater, and the sulfuric-acid band was added 2.5% to the pulp adjusted to Canadian standard freeness (C. S.F) 400ml, and it was referred to as pH5.3. Subsequently, by making into a paper durability agent each copolymer water solution obtained in the example and the example of a comparison, after adding and stirring 0.5% for pulp, pulp slurry concentration was diluted to 0.07%, paper making was carried out and the wet sheet was obtained so that it might become basis-weight 120 g/m² by the TAPPI sheet machine. Press dehydration of this sheet is carried out for 1 minute by 5kg/cm², and it dries for 3 minutes in 105 degrees C with a rotation mold drum dryer. furthermore, JIS after carrying out gas conditioning to the bottom of the condition of 20 degrees C and 65%R.H. for 24 hours P 8112 -- applying correspondingly -- a ratio -- bursting strength was measured. A result is shown in Table 3.

[0033]

[Table 3]

	比破裂強さ
実施例 1	2.48
実施例 2	2.56
実施例 3	2.54
実施例 4	2.61
実施例 5	2.52
実施例 6	2.60
実施例 7	2.63
実施例 8	2.56
実施例 9	2.58
実施例 10	2.53
比較例 1	2.34
比較例 2	2.45
比較例 3	2.48
比較例 4	2.42
ブランク	1.98

[0034]

[Effect of the Invention] As shown in Table 2, while it can control copolymer viscosity in the large range and problems, such as gelation, stop being able to happen easily, the effectiveness which was excellent also in the improvement effectiveness in paper durability as an additive for paper manufacture as shown in Table 3 is demonstrated.

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TECHNICAL FIELD

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PRIOR ART

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EFFECT OF THE INVENTION

[Effect of the Invention] As shown in Table 2, while it can control copolymer viscosity in the large range and problems, such as gelation, stop being able to happen easily, the effectiveness which was excellent also in the improvement effectiveness in paper durability as an additive for paper manufacture as shown in Table 3 is demonstrated.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention is faced obtaining the acrylamide system polymer of the letter of branching which is hypoviscosity though it is the same amount of macromolecules as what is depended on the conventional technique, a polymerization reaction can be controlled more to stability, and the additive for paper manufacture which makes an active principle the polymer which made branching structure homogeneity by this, and demonstrates stable effectiveness to the outstanding paper durability improvement effect and condition fluctuation is offered.

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- 3.In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] this invention persons came to complete a header and this invention for attaining the purpose by using the acrylamide system copolymer obtained by copolymerizing the monomer mixture which contains the methacrylonitrile which shows the chain transfer effectiveness and the bridge formation effectiveness as an indispensable component, as a result of repeating research wholeheartedly, in order to develop the additive for paper manufacture with the stable effectiveness of opposite *Perilla frutescens* (L.) Britton var. *crispa* (Thunb.) Decne. to the water quality of service water, or fluctuation of paper milling pH.

[0008] That is, it is the additive for paper manufacture obtained by copolymerizing (b) water solubility anionic monomer 0.5 - 20-mol % and/or (c) water solubility cationic monomer 0, 5 - 20-mol % and (d) methacrylonitrile 0.05 - ten-mol % monomer mixture (a) acrylamide and/or meta-acrylamide 50 - 9.75-mol%.

[0009] In this invention, the acrylamide or methacrylamide which is the (a) component may be used independently, and may use both together.

[0010] (b) As an example of the water-soluble anionic monomer of a component, the thing of sulfonic-acid systems, such as dicarboxylic acid systems, such as monocarboxylic acid systems, such as an acrylic acid, a methacrylic acid, and a crotonic acid, a maleic acid, a phthalic acid, an itaconic acid, and a citraconic acid, a vinyl sulfonic acid, a styrene sulfonic acid, and 2-acrylamido-2-methyl propane sulfonic acid, is mentioned. This monomer may be a salt and can mention the sodium salt of the various above-mentioned organic acids, potassium salt, etc. as a salt. In addition, these may be used independently, and may mix and use two or more kinds.

[0011] (c) Acrylamide (meta) derivatives, such as acrylic ester (meta) derivative [, such as dialkyl aminoethyl (meta) acrylate which is the monomer which has the third class amino group as an example of the water-soluble cationic monomer of a component, and dialkyl aminopropyl (meta) acrylate,], dialkyl aminopropyl (meta) acrylamide, dialkyl aminopropyl (meta) acrylamide, and acrylamide (meta)-3-methylbutyl dimethylamine, can be mentioned.

[0012] In addition, the water-soluble cationic monomer of (c) The salt of MOMA which has the above-mentioned third class amino group may be used. As such a salt A salt with an inorganic acid like a hydrochloric acid and a sulfuric acid is sufficient, and a salt with an organic acid like a formic acid and an acetic acid is sufficient, and Furthermore, the quaternary salt which formed the third class amino group into 4 class by methyl chloride, low-grade alkyl halide like a methyl bromide, benzyl chloride, aralkyl halide like benzyl bromide, the dimethyl sulfate, epichlorohydrin, etc. is sufficient. Moreover, these (c) components may be used independently, and two or more kinds may be mixed and they may be used.

[0013] the quantitative relation of each above component -- (a) component 99.75 - 50-mol % -- desirable -- 98.9 - 65-mol %, (b) component 0.1 - 20-mol % -- desirable -- 0.5 - 15-mol %, (c) component 0.1 - 20-mol % -- desirable -- 0.5 - 15-mol %, (d) component 0.05 - ten-mol % -- it is 0.1 - five-mol % preferably.

[0014] this invention -- setting -- everything but indispensable component (a) - (d) -- the purpose of this invention -- there -- it is 7, and it is the range and other monomers can be made to contain As such a monomer, there are diacetone acrylamide, acrylic nitril, alkyl acrylate, hydroxy acrylate, vinyl acetate, styrene, alpha methyl styrene, etc. the total mol sum of the

monomer component constituted although the amount of these monomers used changes with properties of each monomer and does not generally have ***** -- receiving -- about 0.1-40 mol % -- it is preferably good about 0.5-30 mol %.

[0015] In this invention, although a cross linking agent is not necessarily needed since the bridge formation effectiveness is done so by the methacrylonitrile itself, it is the range which does not spoil the purpose of this invention, and it is possible to use other cross linking agents together if needed. As such a cross linking agent For example, methylenebis Acrylamide, an ethylene screw (Meta) 2 functionality cross linking agents, such as acrylamide, ethylene GURIKORUJI (meta) acrylamide, diethylene GURIKORUJI (meta) acrylamide, TORIECHIRENGURIKORUJI (meta) acrylamide, a divinylbenzene, and diaryl acrylamide, (Meta) Or polyfunctional cross linking agents, such as 1, 3, 5-thoria chestnut roil hexahydro-S-triazine, triallyl isocyanurate, thoria krill acid pentaerythritol, trimethylol propane acrylate, and diacryloyl imide, N-permutation acrylamide system monomers, such as dimethyl acrylamide, diacetone acrylamide, and isopropyl acrylamide, are mentioned.

[0016] Although the amount used is an amount usually smaller than conditions, and ends and it is 0.005-3-mol % to the total amount of all monomers in order that the bridge formation effectiveness by the methacrylonitrile itself may work, although these cross linking agents can carry out concomitant use use of one sort or the two sorts or more, it is 0.01-1-mol % preferably.

[0017] Moreover, in this invention, although a chain transfer agent is not necessarily needed in order to also commit the chain migration effectiveness by the methacrylonitrile itself, it is possible to use other chain transfer agents together if needed in the range which does not spoil the purpose of this invention. As an example of such a chain transfer agent, the thing of allyl compound systems, such as mercapto systems, such as mercaptoethanol besides isopropyl alcohol, thiourea, thioglycolic acid, mercaptopropionic acid, thiosalicylic acid, thiolactic acid, an aminoethane thiol, thioglycerol, and thiomalic acid, allyl alcohol, allyl compound sulfonic-acid soda, and meta-allyl compound sulfonic-acid soda, is mentioned. in order that these chain transfer agents can carry out concomitant use use of one sort or the two sorts or more and may also commit the chain transfer effectiveness by the methacrylonitrile itself as mentioned above -- an amount with less amount used than this usual kind of reaction condition -- it is -- ending -- the total amount of all monomers -- receiving -- about 0.01-5 mol % -- it is preferably good about 0.03-2 mol %.

[0018] In this invention, various well-known approaches are conventionally applicable as a polymerization method for obtaining a water-soluble polymer. For example, in addition to this, a monomer, a cross linking agent, a chain transfer agent, and water can be taught to a predetermined reaction container said various monomers ((a) - (b) component) and if needed, a polymerization initiator can be added, and the water-soluble target polymer (this may be hereafter called a water-soluble copolymer and a copolymer water solution) can be obtained by warming under stirring. Moreover, while a part or all of a monomer is dropped into a reaction container, it may be made to carry out a polymerization. A catalyst injection can obtain the polymer of the high amount of macromolecules of whenever [branching] by adding a catalyst, although at least 1 time is possible.

[0019] Reaction temperature is about 40-100 degrees C, and reaction time is usually about 0.5 - 8 hours. If it is the radical polymerization initiator usually used in a water solution as a polymerization initiator, it can be used that there is especially no limit, for example, a catalyst is a hydrogen peroxide, a benzoyl peroxide, a peroxide catalyzer like t-butyl peroxide, and persulfuric acid. A bromate catalyst like a persulfate catalyst like ammonium, sodium persulfate, and potassium persulfate, sodium bromate, and a potassium bromate and a fault boron acid chloride catalyst like fault boron acid sodium are mentioned. Moreover, the redox system catalyst and azo system catalyst which combined the sulfite, the hydrogensulfite, the transition-metals salt, the organic amine, etc. with these as a reducing agent can also be used. These may be used independently and may be used combining two or more kinds. the amount of these catalysts used -- the AUW of a monomer -- receiving -- about 0.01-10wt% -- it is about 0.05-3wt% preferably.

[0020] Also about an additional catalyst, although the same thing as a catalyst is usable for a start (the 1st step), it sees from catalyst effectiveness and a cost side, for example, persulfate like ammonium persulfate or sodium persulfate is the optimal. Of course, especially when there are many amounts of survival of the catalyst used for the 1st step, it is not necessary to add. It is 70-95 degrees C often [temperature / the temperature in the case of carrying out the additional polymerization of the prepolymer is 40 degrees C or more, and / making about 15-55 degrees C / reaction / the 1st step of / into an elevated temperature], and preferably, the amount of the additional catalyst used -- 0.01 - 10wt% -- it is 0.05 - 3wt% preferably. A monomer can also be added to this additional catalyst and coincidence if needed. This monomer presentation may be the same as an initial preparation monomer presentation, or may differ.

[0021] In this invention, while resonance stabilization of the radical generated according to the radical catalyst is carried out by the nitrile group of a methacrylonitrile and it carries out chain transfer-work, by forming the point by the abstraction reaction from a methyl group constructing a bridge, it has work of a cross linking agent/chain transfer agent by the methacrylonitrile independent, and does not have generating of rapid thickening, either, and it becomes easy to polymerization control it.

[0022] In addition, the additive for paper manufacture of this invention can introduce branching structure into a polymer, and serves as hypoviscosity comparatively like ** and the acrylamide system polymer of a conventionally well-known bridge formation mold. Usually, although it is compoundable in the range of 5 - 40 % of the weight of solid content concentration, when using it as an additive for paper manufacture, it is desirable to use it by description 15000cps or less, and 5 - 30% of the weight of the range is desirable as solid content concentration. Therefore, the amount of the water used for a polymerization reaction is good to refer to this and to determine it suitably.

[0023] When it is used as an additive for paper manufacture, the copolymer not only demonstrates the paper durability effectiveness and effectiveness high in respect of filterability, but demonstrates stable effectiveness to condition fluctuation of a paper-milling system, while it is the description to obtain easily the copolymer water solution in which hypoviscosity is shown, though this invention is the amount of macromolecules.

[0024]

[Embodiment of the Invention] An example and the example of a comparison are given to below, and this invention is more concretely explained to it. In addition, each of sections and %s is weight criteria as long as there is no special mention.

[0025]

[Example 1] The 50% acrylamide water-solution 256 section, the acrylic-acid 5.8 section, the dimethylaminoethyl methacrylate 3.2 section, the meta-KURORU nitril 1.4 section, and the water 270 section were taught to the 4 opening flask equipped with an agitator, a thermometer, a ring current cooling pipe, and nitrogen gas installation tubing, pH was adjusted to 3.2 with the sulfuric acid, and the oxygen in the system of reaction was removed through nitrogen gas. The inside of a system was made into 40 degrees C, and the ammonium persulfate water-solution 3.4 section and the 1% sodium-hydrogensulfite water-solution 6 section were supplied 10% as a catalyst to the bottom of stirring. After carrying out a temperature up to 90 degrees C, the ammonium persulfate water-solution 3 section was added 10 more%, and temperature was held for 2 hours. The water 110 section was supplied after reaction termination, and the copolymer water solution of pH 3.7, the solid content of 15.4%, the viscosity (25 degrees C) of 7600cps, and weight average molecular weight 2,340,000 was obtained.

[0026]

[Example 1-a] The monomer mixed water solution adjusted like the example 1 was made into 40 degrees C, and the 10% water-solution 5 of 2 of azo system catalyst and 2'-azobis (2-amidinopropane) hydro chloride section was supplied as a catalyst. After solution temperature amounted to 85 degrees C or more, the ammonium persulfate water-solution 4 section was added 10 more%, and this temperature was held for 2 hours. The water 110 section was supplied after reaction termination, and the copolymer water solution of pH4.0, the solid content of 15.7%, the viscosity (25 degrees C) of 8200cps, and weight average molecular weight 2,480,000 was

obtained.

[0027]

[Example 1-b] The monomer mixed liquor adjusted like the example 1 was made into 40 degrees C, and the ammonium persulfate water-solution 6 section was supplied 10% as a catalyst. Solution temperature was held above 85 degrees C for 2 hours. The water 110 section was supplied after reaction termination, and the copolymer water solution of pH3.9, the solid content of 15.6%, the viscosity (25 degrees C) of 4800cps, and weight average molecular weight 1,890,000 was obtained.

[0028]

[Examples 2-10] In the example 1, the class or its operating rate of (a) - (d) component was changed as shown in Table 1, and also the same actuation as an example 1 was performed, and various copolymer water solutions were obtained. the description of the obtained various copolymer water solutions -- Table 2 is shown for a value.

[0029]

[Table 1]

	モノマーの種類および使用割合 (モル%)				架橋剤(d) (モル%)	連鎖移動剤 (モル%)
	(a)成分	(b)成分	(c)成分	成分		
実施例 1	AM 90	AA 4	DM 5	MAN 1		
実施例 2	AM 91.5	IA 3	DMBQ 5	MAN 0.5		IPA 1
実施例 3	AM 92	AA 2	DM 1	MAN 1	MBAM 0.01	
		FA 1	DMBQ 3			
実施例 4	AM 91.6	IA 1	DMAPAA 4	MAN 1.4	DMAM 0.05	
		AA 2				
実施例 5	AM 89	AA 2	DM 3	MAN 2	MBAM 0.01	AS 0.6
		MA 2	DMBQ 2			
実施例 6	AM 91.7	FA 3	DM 5	MAN 0.3	MBAM 0.02	IPA 2
実施例 7	AM 88.8	IA 3	DMBQ 6	MAN 1.2	DMAM 0.1	MAS 0.05
		FA 1				
実施例 8	AM 93.5	IA 2	DM 3.5	MAN 1	DMAM 0.1	AS 0.4
実施例 9	AM 89.3	AA 3	DM 2	MAN 0.7	DMAM 0.2	IPA 2
		FA 3	DMBQ 4			
実施例 10	AM 93.8	IA 1	DMBQ 3	MAN 1.2	MBAM 0.02	MAS 0.1
		MA 1				
比較例 1	AM 92	AA 3	DM 5			IPA 3
比較例 2	AM 93	AA 1	DMBQ 4		MBAM 0.06	IPA 5
		IA 2				
比較例 3	AM 93	IA 2	DMAPAA 3		DMAM 1	AS 1.2
		FA 1	DM 1			
比較例 4	AM 91	AA 2	DM 3		DMAM 0.7	MAS 0.4
		MA 2	DMBQ 2			

[0030]

[The examples 1-4 of a comparison] Moreover, as examples 1-4 of a comparison, the class or its operating rate of (a) - (d) component of an example 1 was changed, as shown in the example of a comparison of Table 1, and also the same actuation as an example 1 was performed, and various copolymer water solutions were obtained. In addition, although the examples 2-4 of a comparison tended to obtain the object 5000cps or more of product viscosity, since they lifting-

came to be easy of rapid thickening and gelation in the second half of a polymerization, they performed viscosity control in the amount of catalysts etc., and obtained the product. the description of the obtained various copolymer water solutions -- Table 2 is shown for a value.

[0031]

[Table 2]

	性 状			
	固形分 (%)	pH	粘度 (cps)	Mw (万)
実施例 1	15.4	3.7	7600	234
実施例 2	15.7	3.9	8700	213
実施例 3	15.2	4.3	9300	257
実施例 4	15.5	4.0	11100	267
実施例 5	15.6	4.1	7600	243
実施例 6	15.3	3.8	3500	231
実施例 7	15.6	3.7	9200	276
実施例 8	15.4	3.9	12300	278
実施例 9	15.3	4.0	7100	226
実施例 10	15.4	4.1	4300	225
比較例 1	15.3	4.0	7800	43
比較例 2	15.4	3.9	3200	165
比較例 3	15.6	4.3	3800	213
比較例 4	15.3	4.1	2800	243

As front Naka and a (a) component, as an AM:acrylamide and (b) component AA:acrylic acid, As an itaconic acid, FA:fumaric acid, and an MA:maleic-acid and (c) component, IA :

DM:dimethylaminoethyl methacrylate, As dimethylaminopropyl acrylamide, the fourth class ghost by the benzyl chloride of DMBQ:DM, and a (d) component, DMAPAA : as MAN:meta-KURORU nitril and a cross-linking monomer MBAM: Methylenebis acrylamide, DMAM: IPA:isopropyl alcohol, MAS:meta-allyl compound sulfonic-acid soda, and AS:allyl compound sulfonic-acid soda are shown as dimethyl acrylamide and a chain transfer agent, respectively.

[0032]

[Performance evaluation] corrugated paper used paper -- a Niagara style -- beating was carried out with the beater, and the sulfuric-acid band was added 2.5% to the pulp adjusted to Canadian standard freeness (C. S.F) 400ml, and it was referred to as pH5.3. Subsequently, by making into a paper durability agent each copolymer water solution obtained in the example and the example of a comparison, after adding and stirring 0.5% for pulp, pulp slurry concentration was diluted to 0.07%, paper making was carried out and the wet sheet was obtained so that it might become basis-weight 120 g/m² by the TAPPI sheet machine. Press dehydration of this sheet is carried out for 1 minute by 5kg/cm², and it dries for 3 minutes in 105 degrees C with a rotation mold drum dryer. furthermore, JIS after carrying out gas conditioning to the bottom of the condition of 20 degrees C and 65%R.H. for 24 hours P 8112 -- applying correspondingly -- a ratio -- bursting strength was measured. A result is shown in Table 3.

[0033]

[Table 3]

	比破裂強さ
実施例 1	2.48
実施例 2	2.56
実施例 3	2.54
実施例 4	2.61
実施例 5	2.52
実施例 6	2.60
実施例 7	2.63
実施例 8	2.56
実施例 9	2.58
実施例 10	2.53
比較例 1	2.34
比較例 2	2.45
比較例 3	2.48
比較例 4	2.42
ブランク	1.98

[Translation done.]